JSB-DP006

Our GC×GC modulators: an overview

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC×GC) is a very powerful separation technique in which the carrier gas eluting from a capillary GC column (first dimension) is introduced onto a second capillary column (second dimension) with different but complementary separation mechanism. This way the sample is subject to two different separation processes within a single analysis. This increases remarkably the peak capacity and leads to an enormous resolving power. Compared to a single column separation, GC×GC can provide highly detailed sample characterization and excellent visualization of sample components.

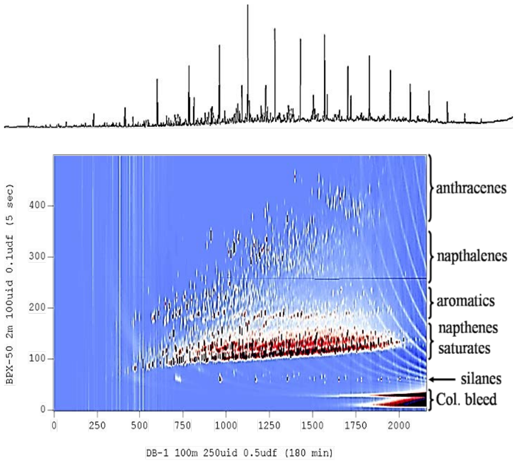

Figure 1 – Example of the excellent resolving power possible with GC×GC

The heart of the system is the modulator. This device continuously fractionates the peaks eluting from the first dimension and re-inject them into the second dimension where further separation occurs. Typically eluting peaks from the first dimension are cut by the modulator into 3-5 pulses. The separation on the second dimension column is very fast, typically 3-8 seconds.

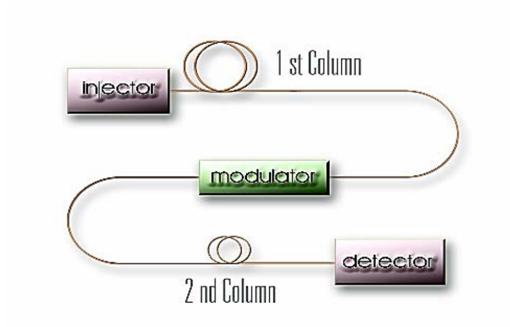

Figure 2 – Schematic representation of a GC×GC system

Nowadays several different types of modulators are available. Some use thermal trapping and focusing to modulate the analytes, while others are valve- or flow-based and fractionate the carrier gas. There is no ideal modulator that is good for all applications. Each design has its own strengths and limitations. Selecting the right modulator is of critical importance because it can affect dramatically the quality of the GC×GC results. This choice should be tailored on your need, taking into consideration the nature of the samples and the types of analyses encountered in your laboratory.

2. Flow modulators

Flow modulators provide modulation without the need for cryogen, making GC×GC accessible and affordable. Moreover, there are no volatility limits for the modulation of volatiles.

2.1. Agilent Differential Flow Modulator

The Agilent Differential Flow Modulator is based on the Agilent Capillary Flow Technology (CFT) and fractionates the carrier gas by simply directing the carrier gas flow. A three-way solenoid valve receives a high supply of gas. The periodic switching of this three-way valve drives the modulator. During the loading step the effluent from the first column fills the collection channel. When the modulation valve is switched a high flow injects the channel content into the second dimension.

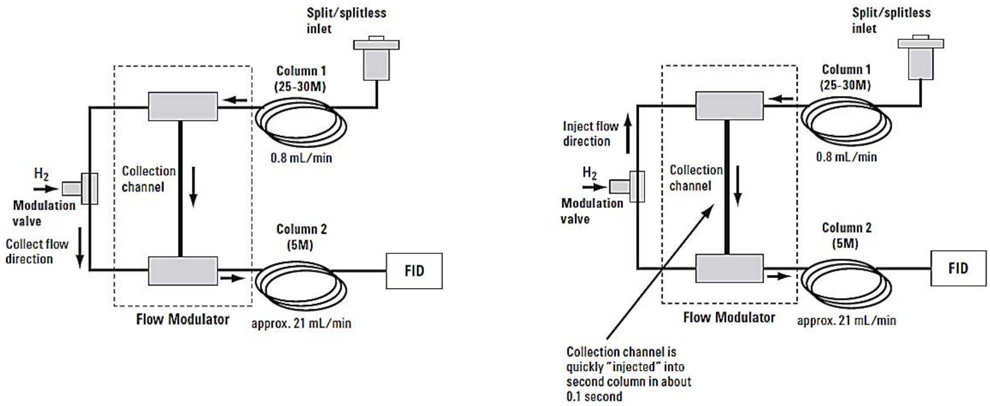

Figure 3 – Schematic of the Agilent Direct Flow Modulator and its loading (left) and injection (right) steps

Key features:

- Forward fill/flush dynamics.
- No liquid nitrogen required.
- Modulation from C1+.
- Fast second dimension re-injection also for very heavy compounds.
- Second dimension outlet flow: ± 20mL/min.
- Fixed collection channel.

Strengths:

- Widest sample range, from gases to high boilers.
- Suitable for thermally labile analytes.
- Installation is simple. Cheap and robust set-up.
- Suitable for routine analyses that do not require frequent set-up changes and for group characterization that does not require the best second dimension resolution.

Limitations:

- Restricted in terms of column dimensions and modulation times.
- Coupling to MS requires splitting of the outlet flow, and thus gives a decrease in sensitivity.
- The forward fill/inject design causes tailing in the second dimension, causing loss in resolution.
- Keen to overload, limited sample capacity range.

Example of application: Routine analysis of Total Petroleum Hydrocarbon (TPH) in soil and water.

Environmental laboratories involved in TPH analysis are required to report a total TPH value, an aliphatic value and an aromatic value. When using conventional GC it is not possible to chromatographically distinguish between the aliphatic and aromatic components and a lengthy and costly splitting process is therefore required. GC×GC with the Agilent differential flow modulation can be used to remove the time consuming, costly and inaccurate aliphatic/aromatic splitting required for traditional TPH analysis with conventional GC. A second method is not required. During data processing, the chromatograms can be processed automatically using predefined templates.

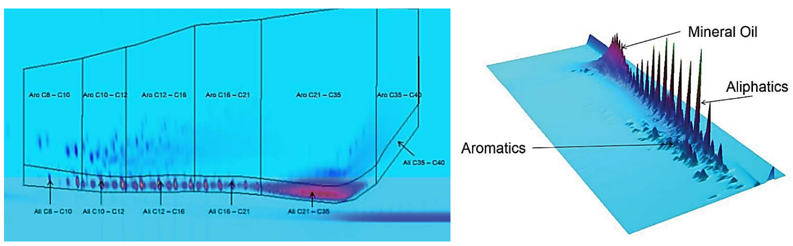

Figure 4 – 2D plot showing aliphatic/aromatic separation and banding (left) and 3D visualization (right)

2.2. Reversed-Inject Flow Modulator

The Reversed Flow Modulator is a second generation flow modulator. The new design reverses flow direction in the channel during the inject part of the modulation cycle. This shows performance benefits over the direct CFT device. The tailing in the second dimension is eliminated, leading to better resolution.

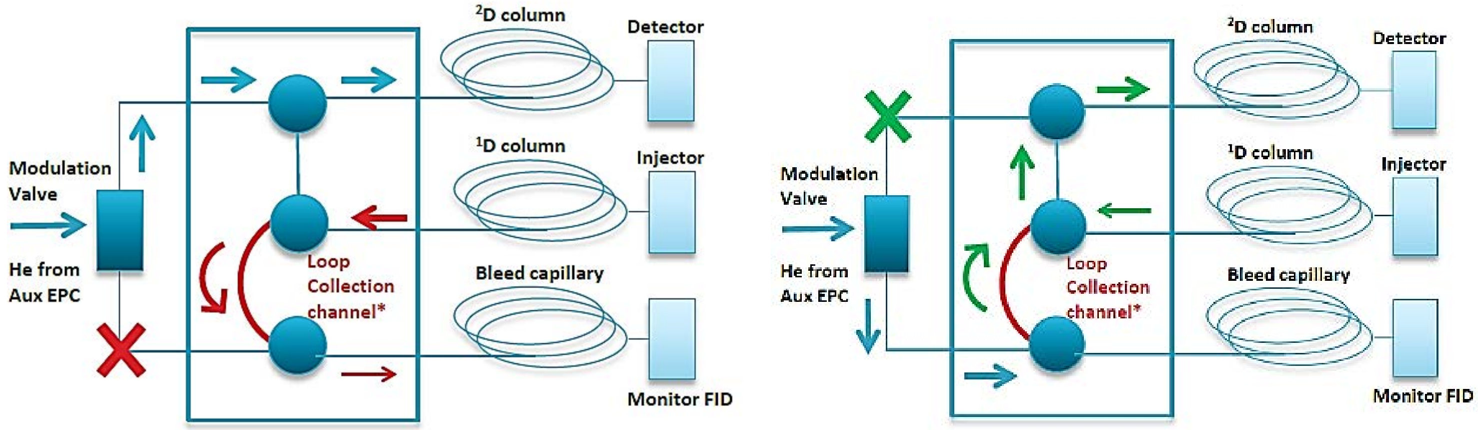

Figure 5 – Schematic of the Reversed Flow Modulator and of its loading (left) and injection (right) steps

Key features:

- Reversed fill/flush dynamics.
- No liquid nitrogen needed.
- Modulation from C_1+.
- Fast second dimension re-injection also for very heavy compounds.
- Adjustable loop collection channel.
- Improved modulated peak symmetry and capacity.
- Second dimension outlet flow: ± 2-8 mL/min.

Strengths:

- It provides the widest sample range, from gases to high boilers (C_{50}+).
- Suitable for thermally labile analytes.
- Improved modulated peak symmetry.
- Ability to handle a higher concentration range of analytes.
- The adjustable accumulation chamber can be optimized providing good flexibility in terms of columns dimensions and modulation times.

Limitations:

- Coupling to MS requires splitting of the outlet flow and will therefore decrease the sensitivity.
- The set-up is rather complex and optimization laborious.
- Rather complex set-up.
- More expensive than the Differential Flow Modulator.

3. Thermal modulators

Thermal modulators are valve-less devices that presents neither dead volumes nor active sites to the analytic path. Thermal modulators use two cryogenic focusing steps and rapid hot re-injection that produce very sharp peaks onto the second dimension. This way the sensitivity and the resolution are significantly enhanced compared to flow modulators. Additional advantages are the possibility to tune freely column dimensions and modulation time and the compatibility to all detectors. In the **Zoex Loop Modulators** the column is configured in a loop so that only one cold and one hot jet are required for double focusing. This minimizes the hardware necessary while granting excellent performance.

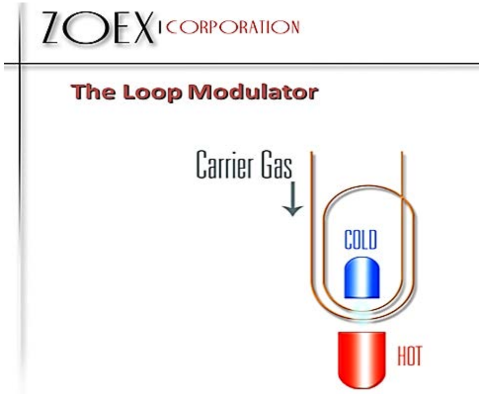

Figure 6 – Schematic representation of a Zoex thermal modulator

3.1. ZX1 Liquid Nitrogen Cooled Loop Modulation System

This model uses a liquid nitrogen bath to cool the gas supplied to the cold jet, granting excellent trapping power.

Figure 7 – The ZX1 Modulation System

Key Features:

- Cold Jet reaches -189 °C.
- Modulation from C_2 to C_{50}.
- Very sharp peaks injected on to the second dimension
- Compatible with all detectors.
- LN_2 supply at 30 psig (206 kPa) required to fill the cold bath–bench top Dewar.
- Auto Fill Unit required for unattended operation.
- N_2 consumption for both hot jet and cold jet: ± 20L/minute.

Strengths:

- Best sensitivity.
- Best second dimension resolution.
- Provides excellent flexibility, suitable for most applications.
- Method development and optimization are very simple.

Limitations:

- Liquid nitrogen consumption.
- Not suitable for compounds lighter than C_2 and heavier than C_{50}.

3.2. ZX2 Closed Cycle Refrigerated Loop Modulation

This model does not require liquid nitrogen for the cold jet but uses a closed cycle refrigeration system, making GC×GC with thermal modulation more accessible and affordable.

Figure 8 – The ZX2 Modulation System

Key Features:

- Cold Jet reaches -91 °C
- Modulation from C_7 to C_{50}
- Very sharp peaks injected on to the second dimension
- Compatible with all detectors
- No liquid cryogen required to create the cold jet
- N_2 consumption for both hot jet and cold jet: ± 20L/minute

Strengths:

- Best sensitivity.
- Best second dimension resolution.
- Provides excellent flexibility, suitable for most applications.
- Method development and optimization are very simple.

Limitations:

- Not suitable for compounds lighter than C_7 and heavier than C_{50}.

Example of application: *Analysis of aging markers in diesel oil by GC×GC-QTOF.*

The composition of diesel oil changes with time as a result of degradation. The major components in a fresh oil are the linear alkanes where branched alkanes become predominant in highly degraded oil. The ratio between heptadecane (n-C_{17}) and 2,6,10,14-tetramethyl-pentadecane (or pristane) has the highest correlation with this process and is used, for instance, for age determination of diesel oil spills in soil by GC. However, this approach is affected by large uncertainty because in mono-dimensional GC the markers are not separated from the matrix. GC×GC with thermal modulation, with its unmatched peak capacity, is a very powerful tool for the detailed separation of highly complex petrochemical samples and therefore for the determination of age markers in diesel.

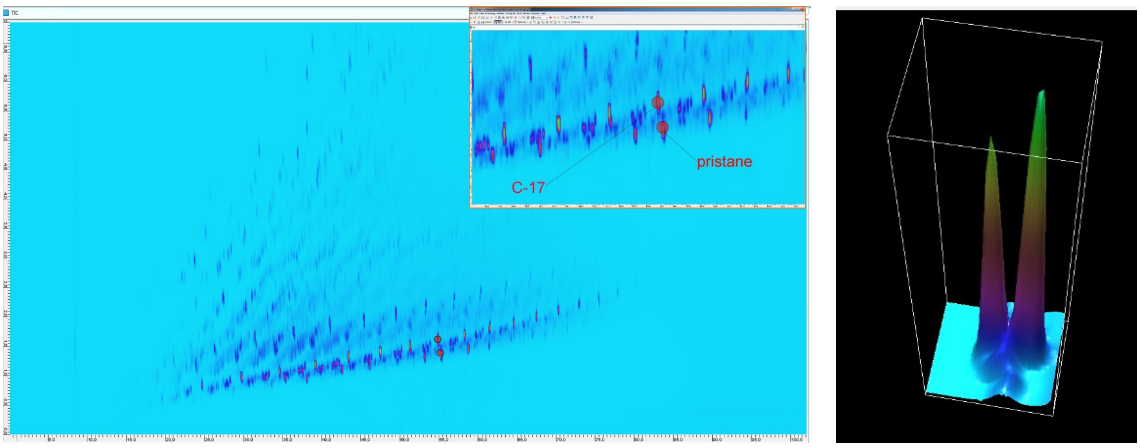

Figure 9 –2D plot of a diesel oil sample (left) and 3D visualization of the separation between n-C_{17} and pristane (right)

4. GC Image

GC×GC data require dedicated software. GC Image is a software package that allows visualization and processing of 2D data in a quick and simple way. The raw data files can be displayed as 2D or 3D plots with a few clicks. Several visual tools are available to help characterizing the 2D plots obtained or compare different samples with or without peak identification. Both qualitative and quantitative results are available. Peaks, groups and textual features can be added to a template which will be applied to future similar samples for a quick, labor-free analysis.

For more details please refer to our application note providing an overview of GC Image and its features.

5. Conclusions

- Every modulator type has several key features that should be taken into consideration when selecting the right GC×GC set-up. The choice of the right should be tailored to your applications, only in this way you can find the perfect modulator for your laboratory!

- Flow modulators are robust and their operation is cheap. The direct flow modulator is very appealing for routine analyses which require minimal changes. The reversed flow modulator grants more flexibility but it is also more complex. They can handle samples of any volatility, from gases to very heavy compounds. Their resolution power is suitable for group analysis but not sufficient for complex separations that require the best resolution in the second dimension.

- The Zoex thermal modulators offer superior performance in terms of high resolution and allow unraveling samples of particularly high complexity. Additionally, they are extremely flexible and very easy and quick to optimize. Like all thermal modulators the volatility range is limited, but the ZX1 with cryogenic modulation is suitable for volatiles as well. These features make them the method of choice for laboratories that need to tackle elevated samples complexity and to be able to deal with a wide range of different applications.

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